Density-Functional Theory for Triplet Superconductors

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Abstract

The density-functional theory of superconductivity is extended to triplet superconductors and superfluid helium 3. We prove a Hohenberg-Kohn-type theorem for these systems and derive effective single-particle equations. The latter include exchange and correlations in a formally exact way and allow the treatment of both electronic and phonon-induced superconductivity. The relation of this approach to the Bogolubov-de Gennes mean-field theory and to phenomenological theories based on Ginzburg-Landau functionals is discussed.

1 Introduction

The purpose of this work is to generalize the density-functional theory (DFT) for superconductors to the case of triplet superconductors.

DFT for superconductors was originally formulated for superconductors with a singlet order parameter [1]. The basis of this theory is provided by a Hohenberg-Kohn (HK) type theorem which states that all properties of a superconducting system can be expressed as functionals of the number density n and the order parameter Δ.

The other basic ingredient is a set of Kohn-Sham (KS) type equations, which allow the determination of the density, the order parameter and the grand canonical potential from single-particle wave functions which are calculated self-consistently. Many-body effects beyond the Hartree (mean field) approximation enter the theory through an exchange-correlation (xc) functional F_{xc} which is a universal functional of the number density and the order parameter. This functional, just as the corresponding normal-state xc functional, is not known exactly.

The formalism has meanwhile been extended to include current densities and external vector potentials [2, 3], the magnetization density and its interaction with magnetic fields [3] and time dependent external fields [4]. The resulting KS equations have been solved using band structure methods with a phenomenological ansatz for the xc functional [5, 6]. As another strategy for the solution of the equations an approximate decoupling into a gap equation and an ordinary normal-state KS equation has been proposed [7, 8].

Recently an LDA-type approximation for the universal xc-functional has been constructed [3, 9] which generalizes the normal-state LDA in taking into account the dependence of the xc functional on the order parameter explicitly. A frequency dependent linear response formalism based on the general theory has also been worked out [10].

All this work has been directed towards inhomogeneous (i.e. short coherence-length) and strongly correlated superconductors, which cannot be treated properly within the BCS theory. The order parameter (OP), which is the basic quantity in this treatment, is

a singlet OP, i.e. of the form

$$\Delta(\mathbf{r},\mathbf{r}') =< \hat{\psi}_{\uparrow}(\mathbf{r})\hat{\psi}_{\downarrow}(\mathbf{r}') > . \tag{1}$$

It is well known, however, that many interesting systems cannot be described adequately with such an OP. The prime example is superfluid helium 3. It is now firmly established that the different phases of helium 3 are characterized by triplet OPs [11]. We will comment on this case in section 4 below.

As far as proper superconductors are concerned, the hypothesis that the OP is actually a triplet OP has been put forward for both the high-temperature superconductors and, in particular, the heavy-fermion systems [12, 13, 14, 15, 16, 17, 18]. In some heavy-fermion superconductors the spin-orbit coupling is very strong, so that the spin is not a good quantum number any more. In this case a theory which consistently takes into account the effect of relativity on the singlet [19] or triplet [20] OP should be employed.

Finally, several models for the coexistence of magnetism and superconductivity involve triplet superconductivity (see e.g. [21, 22, 23] and references therein).

In view of the capability of the DFT approach to treat correlations in inhomogeneous systems it is desirable to extend the formalism of DFT for superconductors to the case of triplet superconductivity.

To this end we start from a Hamiltonian which explicitly contains a triplet OP. Different ways to set up the basic Hamiltonian are presented in section two, where we also discuss the structure and some of the symmetries of the order parameters in some detail. In section three we outline the proofs for the generalized HK and KS theorems. The equations given include both singlet and triplet contributions. In section four we offer some brief comments on available functionals and discuss the application of the formalism to superfluid helium 3.

2 The Hamiltonian for Triplet Superconductors

The Hamiltonian we consider is given by

$$\hat{H} = \hat{T} + \hat{V} + \hat{U} + \hat{W} - \hat{D} \tag{2}$$

Here $\hat{T}$ is the usual operator of the kinetic energy

$$\hat{T} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \, \hat{\psi}^\dagger_\sigma(\mathbf{r}) \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \hat{\psi}_\sigma(\mathbf{r}). \tag{3}$$

$\hat{V}$ contains the external (lattice) potential $v(\mathbf{r})$ and the chemical potential μ.

$$\hat{V} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \, \hat{\psi}^\dagger_\sigma(\mathbf{r}) (v(\mathbf{r}) - \mu) \hat{\psi}_\sigma(\mathbf{r}). \tag{4}$$

$\hat{U}$ represents the Coulomb interaction

$$\hat{U} = \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r \int d^3r' \, \hat{\psi}^\dagger_\sigma(\mathbf{r}) \hat{\psi}^\dagger_{\sigma'}(\mathbf{r}') \frac{q^2}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_\sigma(\mathbf{r}). \tag{5}$$

The last two terms in Eq.(2) are related to superconductivity. $\hat{W}$ is an additional phonon-induced attractive interaction. In the most general case, $\hat{W}$ is given by

$$\hat{W} = - \sum_{\sigma\sigma'\tau\tau'} \int d^3r \int d^3r' \int d^3x \int d^3x' \, \hat{\Delta}_{\sigma'\sigma}(\mathbf{r}', \mathbf{r})^\dagger w_{\sigma\sigma'\tau'\tau}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \hat{\Delta}_{\tau'\tau}(\mathbf{x}, \mathbf{x}') \, , \tag{6}$$

where the OP matrix is defined as

$$\hat{\Delta}_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \hat{\psi}_\sigma(\mathbf{r}) \hat{\psi}_{\sigma'}(\mathbf{r}') \tag{7}$$

which is a straightforward generalization of Eq.(1). $\hat{D}$ finally represents the coupling of the OP matrix to a general spin dependent external pair potential $\tilde{D}_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$.

$$\hat{D} = \sum_{\sigma\sigma'} \int \, d^3r \, d^3r' \, \left[\tilde{D}^*_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \hat{\Delta}_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') + H.c. \right] \tag{8}$$

Physically, this term can be viewed as representing the pair potential of an adjacent superconductor, induced through the proximity effect [1, 2, 3]. Alternatively it can be viewed as a mathematical device to produce eigenfunctions with the correct symmetry (i.e. broken gauge invariance) [23]. If no proximity-induced pair potential is present, $\tilde{D}_{\sigma\sigma'}$ has to be set equal to zero in the final equations.

In the framework of DFT this procedure is well known from spin-DFT, where external magnetic fields are introduced in the beginning to generate a non-vanishing OP which, in this case, is the spin magnetization. For zero external field the final equations then describe spontaneous magnetization forming below T_m, including correlation effects. In

the same way, the case of zero external pair potential in the DFT for superconductors describes superconductivity spontaneously forming below T_c, again including correlations.

The general interaction w which forms the kernel of $\hat{W}$ can be specified according to the particular model for superconductivity under study. One common approximation is

$$w_{\sigma\sigma'\tau'\tau}(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}') = \delta_{\sigma\tau}\delta_{\sigma'\tau'}w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}'). \tag{9}$$

This covers many cases of physical interest in superconductors such as the Bardeen-Pines interaction [3, 24], the local Gorkov interaction [25] and the original model interaction of BCS [26]. For the case of purely electronic superconductivity, which has been suggested to be present in the high-temperature superconductors, w can be taken to be zero since the Coulomb interaction is already included in $\hat{H}$ through $\hat{U}$.

The crucial step in any DFT is the identification of those 'densities' in terms of which HK and KS theorems can be formulated. Although, in our case, a DFT can be established in terms of the quantities $\Delta_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$ it is preferable to work with another set of 'densities' which exhibit the singlet and triplet character explicitly. To this end we have to rewrite Eq.(8) in terms of the new densities.

The standard way of separating the singlet and triplet components is by using the Balian-Werthamer parametrization [12, 27, 28]. We write out the spin sum in Eq.(8) explicitly and go over to a spinor notation. This results in

$$\hat{D} = \int d^3r d^3r' \Psi^T(\mathbf{r}) \left[\tilde{D}^*_{\uparrow\uparrow} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \tilde{D}^*_{\uparrow\downarrow} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + \tilde{D}^*_{\downarrow\uparrow} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + \tilde{D}^*_{\downarrow\downarrow} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \right] \Psi(\mathbf{r}') + H.c. \tag{10}$$

Here $\Psi(\mathbf{r})$ is a two-component spinor defined as $(\hat{\psi}_\uparrow(\mathbf{r}), \hat{\psi}_\downarrow(\mathbf{r}))^T$. Upon setting

$\tilde{D}_s = \tilde{D}_{\uparrow\downarrow} - \tilde{D}_{\downarrow\uparrow}$, $\tilde{D}_x = \tilde{D}_{\downarrow\downarrow} - \tilde{D}_{\uparrow\uparrow}$, $\tilde{D}_y = i(\tilde{D}_{\downarrow\downarrow} + \tilde{D}_{\uparrow\uparrow})$, $\tilde{D}_z = \tilde{D}_{\uparrow\downarrow} + \tilde{D}_{\downarrow\uparrow}$, we obtain

$$\hat{D} = \frac{1}{2} \int d^3r\, d^3r'\, \Psi^T(\mathbf{r}) \left[\hat{S}\tilde{D}^*_s(\mathbf{r},\mathbf{r}') + \hat{T}_x\tilde{D}^*_x(\mathbf{r},\mathbf{r}') + \hat{T}_y\tilde{D}^*_y(\mathbf{r},\mathbf{r}') + \hat{T}_z\tilde{D}^*_z(\mathbf{r},\mathbf{r}') \right] \Psi(\mathbf{r}') + H.c. \tag{11}$$

Here $\hat{S} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$, $\hat{T}_x = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$, $\hat{T}_y = i \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and $\hat{T}_z = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

$\tilde{D}_s$ is the pair field of a singlet superconductor (the corresponding matrix is antisymmetric in spin space) while the $\tilde{D}_x$, $\tilde{D}_y$, $\tilde{D}_z$ are the pair fields for triplet superconductors

(with spin-space symmetric matrices). The matrices $\hat{S}$, $\hat{T}_x$, $\hat{T}_y$, $\hat{T}_z$ are those used in the conventional Balian-Werthamer parametrization for triplet states [12, 27, 28]. This representation has the advantage of being well suited to derive generalizations, e.g., to incorporate relativistic effects [19, 20]. However, from the matrix notation of Eq.(11) the Hamiltonian employed in the DFT for singlet superconductors is not easily recovered. Therefore we shall use yet another representation of Eq.(8) for the DFT formulation. We first observe that, as a consequence of the fermionic anticommutation relations, the OP (7) satisfies

$$\hat{\Delta}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}') = -\hat{\Delta}_{\sigma'\sigma}(\mathbf{r}',\mathbf{r}). \tag{12}$$

The pair fields $\tilde{D}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$ in Eq.(8) do not have a definite symmetry under exchange of $\mathbf{r}$ and $\mathbf{r}'$. However, $\tilde{D}_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}')$ and $\tilde{D}_{\downarrow\downarrow}(\mathbf{r},\mathbf{r}')$ can be assumed to be antisymmetric without restriction because, as a consequence of (12), a symmetric component would not contribute to the integral on the right-hand side of Eq.(8). For the up-down components we define symmetric and antisymmetric linear combinations $D_s(\mathbf{r},\mathbf{r}') := \frac{1}{2}(\tilde{D}_s(\mathbf{r},\mathbf{r}') + \tilde{D}_s(\mathbf{r}',\mathbf{r}))$ and $D_0(\mathbf{r},\mathbf{r}') := \frac{1}{2}(\tilde{D}_z(\mathbf{r},\mathbf{r}') - \tilde{D}_z(\mathbf{r}',\mathbf{r}))$. Defining the symmetric and antisymmetric OPs by

$$\hat{\Delta}_s(\mathbf{r},\mathbf{r}') := \frac{1}{2}(\hat{\Delta}_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}') + \hat{\Delta}_{\uparrow\downarrow}(\mathbf{r}',\mathbf{r})) \tag{13}$$

$$\hat{\Delta}_0(\mathbf{r},\mathbf{r}') := \frac{1}{2}(\hat{\Delta}_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}') - \hat{\Delta}_{\uparrow\downarrow}(\mathbf{r}',\mathbf{r})) \tag{14}$$

$$\hat{\Delta}_+(\mathbf{r},\mathbf{r}') := \hat{\Delta}_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}') \tag{15}$$

$$\hat{\Delta}_-(\mathbf{r},\mathbf{r}') := \hat{\Delta}_{\downarrow\downarrow}(\mathbf{r},\mathbf{r}'), \tag{16}$$

Eq.(8) can be rewritten as

$$\begin{aligned}\hat{D} = \int d^3r\, d^3r' \, \Big[&\hat{\Delta}_s(\mathbf{r},\mathbf{r}')D_s^*(\mathbf{r},\mathbf{r}') + \hat{\Delta}_+(\mathbf{r},\mathbf{r}')D_+^*(\mathbf{r},\mathbf{r}') \\ &+\hat{\Delta}_0(\mathbf{r},\mathbf{r}')D_0^*(\mathbf{r},\mathbf{r}') + \hat{\Delta}_-(\mathbf{r},\mathbf{r}')D_-^*(\mathbf{r},\mathbf{r}')\Big] + H.c\end{aligned} \tag{17}$$

where we have defined $D_+ := \tilde{D}_{\uparrow\uparrow}$ and $D_- := \tilde{D}_{\downarrow\downarrow}$. What has been achieved by this final rewriting is that both the pair potentials and the order parameters are even functions for the singlet and odd functions for the triplet contributions. In this way we have incorporated the exactly known symmetry properties of the order parameters. The formulation of a DFT

in terms of Δ_s, Δ_+, Δ_0, Δ_- will facilitate the construction of suitable xc functionals with correct symmetry properties. In terms of these 'densities' the phonon-induced interaction reads

$$\hat{W} = - \sum_{\substack{i,j \in \\ (s,+,0,-)}} \int d^3r \int d^3r' \int d^3x \int d^3x' \hat{\Delta}_i^*(\mathbf{r}', \mathbf{r}) w_{ij}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \hat{\Delta}_j(\mathbf{x}, \mathbf{x}'), \tag{18}$$

where the $w_{ij}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}')$ are given in terms of the $w_{\sigma\sigma'\tau'\tau}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}')$ as follows:

$$\begin{aligned}
w_{++} &= w_{\uparrow\uparrow\uparrow\uparrow} & w_{+0} &= w_{\uparrow\uparrow\uparrow\downarrow} + w_{\uparrow\uparrow\downarrow\uparrow} \\
w_{+-} &= w_{\uparrow\uparrow\downarrow\downarrow} & w_{+s} &= w_{\uparrow\uparrow\uparrow\downarrow} - w_{\uparrow\uparrow\downarrow\uparrow} \\
w_{0+} &= w_{\downarrow\uparrow\uparrow\uparrow} + w_{\uparrow\downarrow\uparrow\uparrow} & w_{00} &= w_{\downarrow\uparrow\uparrow\downarrow} + w_{\downarrow\uparrow\downarrow\uparrow} + w_{\uparrow\downarrow\ u\downarrow} + w_{\uparrow\downarrow\downarrow\uparrow} \\
w_{0-} &= w_{\downarrow\uparrow\downarrow\downarrow} + w_{\uparrow\downarrow\downarrow\downarrow} & w_{0s} &= w_{\downarrow\uparrow\uparrow\downarrow} - w_{\downarrow\uparrow\downarrow\uparrow} + w_{\uparrow\downarrow\uparrow\downarrow} - w_{\uparrow\downarrow\downarrow\uparrow} \\
w_{-+} &= w_{\downarrow\downarrow\downarrow\downarrow} & w_{-0} &= w_{\downarrow\downarrow\uparrow\downarrow} + w_{\downarrow\downarrow\downarrow\uparrow} \\
w_{--} &= w_{\downarrow\downarrow\downarrow\downarrow} & w_{-s} &= w_{\downarrow\downarrow\uparrow\downarrow} - w_{\downarrow\downarrow\downarrow\uparrow} \\
w_{s+} &= w_{\downarrow\uparrow\uparrow\uparrow} - w_{\uparrow\downarrow\uparrow\uparrow} & w_{s0} &= w_{\downarrow\uparrow\uparrow\downarrow} + w_{\downarrow\uparrow\downarrow\uparrow} - w_{\uparrow\downarrow\uparrow\uparrow} - w_{\uparrow\downarrow\downarrow\uparrow} \\
w_{s-} &= w_{\downarrow\uparrow\downarrow\downarrow} - w_{\uparrow\downarrow\downarrow\downarrow} & w_{ss} &= w_{\downarrow\uparrow\uparrow\downarrow} - w_{\downarrow\uparrow\downarrow\uparrow} - w_{\uparrow\downarrow\uparrow\downarrow} + w_{\uparrow\downarrow\downarrow\uparrow}.
\end{aligned}$$

3 Fundamental Theorems

The fundamental theorem of any DFT is the Hohenberg-Kohn theorem. In exactly the same manner as for the normal state [29, 30] or for singlet superconductors [1, 2, 3] one can prove a HK theorem for the Hamiltonian (2) with (17) and (18). For systems at finite temperature the theorem comprises the three statements[1] :

1. The mapping of the set of densities $\{n(\mathbf{r}), \Delta_s(\mathbf{r}, \mathbf{r}'), \Delta_+(\mathbf{r}, \mathbf{r}'), \Delta_0(\mathbf{r}, \mathbf{r}'), \Delta_-(\mathbf{r}, \mathbf{r}')\}$ onto the statistical operators $\hat{\rho} = exp[-\beta(\hat{H})]$ is one-to-one. Since the statistical operator contains the complete information on the system, this means that the above set of densities determine *the entire physics of the system* at thermal equilibrium.

2. The grand canonical potential Ω can be split up into one contribution, Ω_{ext}, from the interaction with the external fields $(v(\mathbf{r}) - \mu)$, $D_s(\mathbf{r}, \mathbf{r}')$, $D_0(\mathbf{r}, \mathbf{r}')$, $D_+(\mathbf{r}, \mathbf{r}')$ and $D_-(\mathbf{r}, \mathbf{r}')$ and one contribution, F, which contains the kinetic energy, the entropy and the interactions $\hat{U}$ and $\hat{W}$:

$$\Omega[n(\mathbf{r}), \{\Delta\}] = \Omega_{ext} + F[n(\mathbf{r}), \{\Delta\}]. \tag{19}$$

[1] Quantities without a caret denote the expectation value of the corresponding operator in thermal equilibrium, e.g., $\Delta =< \hat{\Delta} >$.

F is a *universal* functional of the set of densities, i.e. for *given* particle-particle interactions $\hat{U}$ and $\hat{W}$, the functional F does not depend on the *external* fields.

3. The grand canonical potential taken as a functional of the above set of densities is minimized by the equilibrium densities.

The functional $F[n(\mathbf{r}), \{\Delta\}]$ can be rewritten as

$$\begin{aligned} &F[n, \{\Delta\}] = \\ &T_s[n, \{\Delta\}] - \frac{1}{\beta} S_s[n, \{\Delta\}] + \frac{q^2}{2} \int d^3r \int d^3r' \, \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + F_{xc}^{\beta}[n, \{\Delta\}] \\ &- \sum_{\substack{i,j \in \\ (s,+,0,-)}} \int d^3r \int d^3r' \int d^3x \int d^3x' \Delta_i^*(\mathbf{r}', \mathbf{r}) w_{ij}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta_j(\mathbf{x}, \mathbf{x}'). \end{aligned} \tag{20}$$

Here $\{\Delta\}$ denotes the set of OPs $(\Delta_s, \Delta_+, \Delta_0, \Delta_-)$, β stands for $1/k_B\theta$ and T_s and S_s are the kinetic energy and entropy of non-interacting particles, respectively. Eq.(20) serves as a definition of the universal exchange and correlation functional $F_{xc}^{\beta}[n, \{\Delta\}]$.

At zero temperature one obtains the same three statements with the ground-state energy in place of the grand canonical potential and the ground-state wave function in place of the statistical operator.

To construct Kohn-Sham single-particle equations we use the generalized Bogolubov-Valatin transformation

$$\Psi_\tau(\mathbf{r}) = \sum_{k\sigma} \left(u_{\tau k\sigma}(\mathbf{r}) \gamma_{k\sigma} + v_{\tau k\sigma}^*(\mathbf{r}) \gamma_{k\sigma}^\dagger \right). \tag{21}$$

The KS Hamiltonian $\hat{H}^{(s)}$, i.e. the noninteracting counterpart of the Hamiltonian (2) with the external fields replaced by effective fields $v^{(s)}$ and $D^{(s)}$,

$$\begin{aligned} \hat{H}^{(s)} = &\sum_{\sigma=\uparrow\downarrow} \int d^3r \, \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \hat{\psi}_\sigma(\mathbf{r}) + \sum_{\sigma=\uparrow\downarrow} \int d^3r \, \hat{\psi}_\sigma^\dagger(\mathbf{r}) (v^{(s)}(\mathbf{r}) - \mu) \hat{\psi}_\sigma(\mathbf{r}) \\ &- \int d^3r \, d^3r' \Big[\Big(\hat{\Delta}_s(\mathbf{r}, \mathbf{r}') D_s^{(s)*}(\mathbf{r}, \mathbf{r}') + \hat{\Delta}_-(\mathbf{r}, \mathbf{r}') D_-^{(s)*}(\mathbf{r}, \mathbf{r}') + \\ &\hat{\Delta}_0(\mathbf{r}, \mathbf{r}') D_0^{(s)*}(\mathbf{r}, \mathbf{r}') + \hat{\Delta}_+(\mathbf{r}, \mathbf{r}') D_+^{(s)*}(\mathbf{r}, \mathbf{r}') \Big) + H.c. \Big] \end{aligned} \tag{22}$$

can be diagonalized by the unitary and canonical transformation (21) provided that the coefficients in the transformation satisfy the following set of coupled differential equations

$$\begin{pmatrix} \hat{h} & \mathcal{D} \\ -\mathcal{D}^* & -\hat{h} \end{pmatrix} \begin{pmatrix} u_{k\sigma}(\mathbf{r}) \\ v_{k\sigma}(\mathbf{r}) \end{pmatrix} = E_{k\sigma} \begin{pmatrix} u_{k\sigma}(\mathbf{r}) \\ v_{k\sigma}(\mathbf{r}) \end{pmatrix}. \tag{23}$$

This is the KS equation for triplet superconductors. $u_{k\sigma}(\mathbf{r})$ and $v_{k\sigma}(\mathbf{r})$ are two-component spinors with entries $u_{\tau k\sigma}(\mathbf{r})$ and $v_{\tau k\sigma}(\mathbf{r})$, respectively. Eq.(23) is thus a 4×4 matrix equation. $\hat{h}$ is defined by

$$\hat{h} = I\left(-\frac{\hbar^2\nabla^2}{2m} + v^{(s)}(\mathbf{r}) - \mu\right) \tag{24}$$

where I is the 2×2 unit matrix in spin-space. $\mathcal{D}$ stands for the integral operator

$$\mathcal{D} = \int d^3r' \cdots \hat{d}(\mathbf{r}, \mathbf{r}') \tag{25}$$

The kernel of $\mathcal{D}$ contains the individual contributions of the order parameters for singlet and triplet superconductivity:

$$\hat{d}(\mathbf{r}, \mathbf{r}') = \hat{S}D_s^{(s)}(\mathbf{r}, \mathbf{r}') + \hat{T}_- D_-^{(s)}(\mathbf{r}, \mathbf{r}') + \hat{T}_0 D_0^{(s)}(\mathbf{r}, \mathbf{r}') + \hat{T}_+ D_+^{(s)}(\mathbf{r}, \mathbf{r}') \tag{26}$$

where

$$\hat{S} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad \hat{T}_0 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \hat{T}_z \quad \hat{T}_- = 2\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad \hat{T}_+ = 2\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{27}$$

By construction, the pair potentials $D^{(s)}$ have the same parity as their interacting counterparts, i.e., $D_s^{(s)}(\mathbf{r}, \mathbf{r}') = +D_s^{(s)}(\mathbf{r}', \mathbf{r})$ and $D_i^{(s)}(\mathbf{r}, \mathbf{r}') = -D_i^{(s)}(\mathbf{r}', \mathbf{r})$ with $i \in (0, +, -)$.

The effective single-particle potentials which appear in (24) and (26) are defined as

$$D_i^{(s)}(\mathbf{r}, \mathbf{r}') = D_i(\mathbf{r}, \mathbf{r}') + (-1)^p \sum_j \int d^3x \int d^3x' w_{ij}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}')\Delta_j(\mathbf{x}, \mathbf{x}') + (-1)^p D_{xc,i}[n, \{\Delta\}](\mathbf{r}', \mathbf{r}) \tag{28}$$

where $i, j \in (s, 0, +, -)$ and

$$v^{(s)}[n, \{\Delta\}](\mathbf{r}) = v(\mathbf{r}) + q^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}^{\beta}[n, \{\Delta\}](\mathbf{r}) \tag{29}$$

Here $p = 0$ for singlet superconductivity (i.e. for $i = s$) and $p = 1$ for triplet superconductivity (i.e. for $i \in (0, +, -)$). Equations (28) and (29) follow, as usual, from the application of the HK variational theorem (statement 3 above) to the original interacting system and to a non-interacting reference system with the same densities. The xc-potentials in Eqs.(28) and (29) are formally defined as functional derivatives:

$$v_{xc}^{\beta}[n, \{\Delta\}](\mathbf{r}) = \frac{\delta F_{xc}^{\beta}[n, \{\Delta\}]}{\delta n(\mathbf{r})} \tag{30}$$

$$D_{xc,i}(\mathbf{r},\mathbf{r}') = -\frac{\delta F_{xc}^{\beta}[n,\{\Delta\}]}{\delta\Delta_i^*(\mathbf{r},\mathbf{r}')}. \tag{31}$$

The factor $(-1)^p$ in Eq.(28) has physical significance. Since a large pair potential is favorable for the stability of superconductivity, the signs of the double integral over w_{ij} and of the xc-contribution determine if the last two terms stabilize superconductivity in the singlet or the triplet channel. The BCS model interaction, in particular, employs an everywhere positive spin-independent w and the Hartree-type term in (28) will thus enhance superconductivity in the singlet channel and weaken it in the triplet channel. The same applies for the Gorkov and the Bardeen-Pines interaction, which are of the form (9).

We can thus conclude, without any explicit calculation, that the phonon-mediated interactions usually considered (Bardeen-Pines, Gorkov, BCS-model) are not likely to produce triplet superconductivity, in agreement with experimental facts.

These remarks do not apply to the case of purely electronic superconductivity because for this case $w = 0$. Purely electronic superconductivity would manifest itself in the form of the functionals $D_{xc,i}[n,\{\Delta\}](\mathbf{r},\mathbf{r}')$ and $v_{xc}[n,\{\Delta\}](\mathbf{r})$ and may very well give rise to triplet superconductivity.

The solutions of the above KS equations determine the densities through

$$n(\mathbf{r}) = \sum_{\tau k\sigma}\Big[|u_{\tau k\sigma}|^2 f_\beta(E_{k\sigma}) + |v_{\tau k\sigma}|^2(1-f_\beta(E_{k\sigma})\Big] \tag{32}$$

and

$$\Delta_{\tau\tau'}(\mathbf{r},\mathbf{r}') = \sum_{k\sigma}\left[u_{\tau k\sigma}(\mathbf{r})v^*_{\tau' k\sigma}(\mathbf{r}')(1-f_\beta(E_{k\sigma})) + v^*_{\tau k\sigma}(\mathbf{r})u_{\tau' k\sigma}(\mathbf{r}')f_\beta(E_{k\sigma})\right] \tag{33}$$

where f_β is the Fermi distribution

$$f_\beta(E) = \frac{1}{1+e^{\beta E}}\,. \tag{34}$$

Equations (23) to (33) have to be solved self consistently.

In the local ($\Delta(\mathbf{r},\mathbf{r}') \to \delta(\mathbf{r}-\mathbf{r}')\Delta(\mathbf{r})$) and singlet-only ($\Delta_{0,+,-} \equiv 0$) limit the above equations reduce exactly to those of DFT for singlet superconductors of Ref.[2], while the nonlocal singlet case coincides with the formalism put forward in Ref.[1].

Eq.(33) allows one to calculate the real space order parameter including its dependence on both spatial coordinates. This amounts to the possibility of determining the symmetry of the order parameters for a given system (i.e. a given interaction $\hat{W}$) through approximate solution of the KS equations. The parametric dependence on $\beta = \frac{1}{k_B \theta}$ allows one to determine the temperature dependence of the order parameters and thus in particular the critical temperature.

The equilibrium value of the grand canonical potential $\Omega = \Omega_{ext} + F[n, \Delta]$ can be evaluated immediately, once the equilibrium densities are known. It is given by

$$\Omega = \Omega_s + F_{xc} - \int d^3r n(\mathbf{r}) v_{xc}(\mathbf{r}) + \left[\int d^3r d^3r' \sum_i \Delta_i(\mathbf{r}, \mathbf{r}') D^*_{xc,i}(\mathbf{r}, \mathbf{r}') + c.c. \right]$$
$$- \frac{q^2}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r d^3r' d^3x d^3x' \sum_{ij} \Delta^*_i(\mathbf{r}', \mathbf{r}) w_{ij}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta_j(\mathbf{x}, \mathbf{x}'). \quad (35)$$

To derive Eq.(35) we used that

$$\Delta_i(\mathbf{r}, \mathbf{r}') = (-1)^p \Delta_i(\mathbf{r}', \mathbf{r}) \quad (36)$$

and

$$w_{ij}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}')^* = w_{ji}(\mathbf{x}', \mathbf{x}, \mathbf{r}', \mathbf{r}) \quad (37)$$

which is a consequence of the hermiticity of $\hat{W}$ (c.f. Eq.(18)). Since the grand potential is given by (35) in terms of the particle density and the order parameters, this offers a possibility to compare various order parameters with respect to the energetic stability of the corresponding phase. In contrast to standard Ginzburg-Landau theory, one does not minimize a phenomenological functional, but rather a first-principles density functional whose validity is not limited to the vicinity of T_c.

4 Remarks on Functionals and Applications

4.1 Available Functionals

The DFT formalism described above is formally exact. Any actual application requires an approximation for the xc functional $F^{\beta}_{xc}[n(\mathbf{r}), \{\Delta(\mathbf{r}, \mathbf{r}')\}]$.

In the case of singlet superconductors several such approximations exist: (i) a phenomenological approximation developed by Gyorffy and coworkers [5, 6], (ii) a first prin-

ciples LDA-type approximation [3, 9] and (iii) gradient corrected functionals [31]. For triplet superconductors no explicit functionals exist up to now.

The phenomenological approach, however, can be generalized straightforwardly to the triplet case, because the detailed structure of the OP does not enter the functional in this method.

Any parameter-free first-principles functional such as the LDA or gradient corrected functionals should differ from the corresponding singlet functional because the correlations will in general not be the same for the singlet as for the triplet case. The construction of such functionals for triplet superconductors is possible along the same lines as in the singlet case [3, 9, 31] and remains a project for the future.

4.2 Potential Applications in the Theory of Superfluid Helium 3

Liquid helium 3 undergoes a phase transition into a superfluid state below about 3mK. In this state the individual helium atoms form Cooper pairs, just as the electrons do in the superconducting case [11]. The superfluid state can be described in terms of an order parameter which is very similar to the order parameter describing superconductivity.

The main difference to the case of conventional (BCS) superconductors is the OP symmetry. For helium 3 it is well known that the Cooper pair is in a spin-triplet p-wave state.

The density-functional formalism presented above can be applied to superfluid helium 3 with only minor modifications. The field operators in the original Hamiltonian (2)-(8) have to be reinterpreted as creation and destruction operators for helium atoms instead of electrons. The order parameter is still given by Eq.(7), and all the symmetry arguments discussed in section 2 apply.

The external potential $v(\mathbf{r})$ can be set equal to zero, since there is no analogue to the crystal lattice in the case of helium 3. However, one has to keep $v(\mathbf{r})$ in the derivation, and set it equal to zero only in the final Eq.(29). It then serves as a mathematical device to generate the exchange-correlation potential v_{xc}, just as $D(\mathbf{r}, \mathbf{r}')$ is a device to generate $D_{xc}(\mathbf{r}, \mathbf{r}')$.

Finally, and most importantly, the Coulomb interaction has to be replaced by the interaction between helium 3 atoms. For this one can use the potentials discussed within the framework of paramagnon theory or Fermi liquid theory [11, 32] or any other parametrization of the interaction between the atoms.

Density-functional theory for superfluid helium 3 could then constitute a tool to treat inhomogeneities in the superfluid state such as the effects of surfaces, textures and impurities. Similar effects in metals have been treated very successfully within the framework of ordinary density-functional theory.

Another virtue of the theory is that minimization of the grand potential through iterative solution of the KS equations will, just as for electrons, provide a means to test OPs of various symmetries with respect to their energetic stability.

4.3 Generalizations and Further Applications

A particularly interesting application of the formalism would be the interface between a singlet and a triplet superconductor. In this case the external pair potentials immediately acquire physical significance. It has been demonstrated by explicit construction that for singlet superconductors the DFT formalism is well suited to treat interfaces between different superconductors [1]. On the experimental side, the study of such singlet-triplet interfaces has been suggested as a means to investigate the parity of the heavy fermion superconductors (see Ref.[27] and references therein). Although matters are complicated through the spin-orbit interaction in the heavy fermion compounds, this might be a promising situation on which the above formalism could be applied directly.

An interesting generalization of the above work would be to include the effect of magnetic fields. This is important, e.g., for the high temperature superconductors, the heavy fermion systems and the magnetic superconductors. In all these systems, the presence of a triplet contribution to the OP is possible (and in some cases even likely) while the phase diagrams suggest the importance of magnetic correlations for the superconducting state.

Finally, it is well known that in heavy fermion superconductors spin-orbit effects are very strong. This makes a classification in singlet and triplet OPs somewhat questionable.

One has to resort either to a classification with respect to parity [13] or to a relativistic treatment [19]. Since the recently developed relativistic theory of superconductivity [19] revealed the presence of interesting new spin-orbit terms in superconductors, it is desirable to generalize this theory to triplet superconductors as well.

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References

[1] L.N. Oliveira, E.K.U. Gross, W. Kohn, Phys. Rev. Lett. **60**, 2430 (1988).

[2] W. Kohn, E.K.U. Gross, L.N. Oliveira, J.de Physique **50**, 2601 (1989).

[3] E.K.U. Gross, S. Kurth, K. Capelle and M. Lüders in *Density-Functional Theory*, eds. R.M. Dreizler, E.K.U. Gross (Plenum, New York 1995).

[4] O.-J. Wacker, R. Kümmel, E.K.U. Gross, Phys. Rev. Lett. **73**, 2915 (1994).

[5] M.B. Suvasini, W.M. Temmerman, B.L. Gyorffy, Phys.Rev. **B 48** 1202 (1993).

[6] M.B. Suvasini, B.L. Gyorffy, Physica **B 195** 109 (1992).

[7] E.K.U. Gross, S. Kurth, Int. J. Quant. Chem. Symp. **25**, 289 (1991).

[8] S. Kurth, K. Capelle, M. Lüders, E.K.U. Gross, to be published.

[9] S. Kurth, E.K.U. Gross, to be published.

[10] M. Lüders, E.K.U. Gross, Int. J. Quant. Chem. Symp., (1995), in press.

[11] D. Vollhardt, P. Woelfle, *The superfluid Phases of Helium 3*, Taylor&Francis, (1990).

[12] P. Fulde, J. Keller, G. Zwicknagl, Sol. Stat. Phys. **41**, 1, (1988).

[13] P.W. Anderson, Phys. Rev. **B 30**, 1549 and 4000 (1984).

[14] K.S. Bedell, K.F. Quader, Phys. Rev. **B 32**, 3296 (1985).

[15] S. Han, K.W. Ng, E.L. Wolf, A. Millis, J.L. Smith and Z. Fisk, Phys. Rev. Lett. **57** 238, (1986).

[16] C. Choi, J. Sauls, Phys. Rev. Lett. **66**, 484, (1991).

[17] H.R. Ott, H. Rudigier, T.M. Rice, K. Ueda, J.L. Smith, Phys. Rev. Lett. **52**, 1915, (1984).

[18] M.R. Norman, Phys. Rev. Lett. **72**, 2077, (1994).

[19] K. Capelle, E.K.U. Gross, Phys. Lett. **A 198**, 261, (1995).

[20] K. Capelle, E.K.U. Gross, to be published.

[21] K.P. Sinha, S.L. Kakani, *Magnetic Superconductors* (Nova Science Publishers, New York, 1989).

[22] Yu.A. Izumov, Yu.N. Skrjabin, Phys. Stat. Sol. **B61**, 9, (1974).

[23] S.V. Vonsovsky, Yu.A. Izymov, E.Z. Kurmaev, *Superconductivity of Transition Metals*, (Springer-Verlag, 1982).

[24] J. Bardeen, D. Pines, Phys. Rev. **99**, 1140, (1955).

[25] L.P. Gorkov, Sov.Phys. JETP **7**, 505, (1958).

[26] J.Bardeen, L.N.Cooper, J.R.Schrieffer, Phys.Rev. **108**, 1175, (1957).

[27] M. Sigrist, K. Ueda, Rev. Mod. Phys. **63**, 239, (1991).

[28] R. Balian, N.R. Werthamer, Phys.Rev. **131**, 1553, (1963).

[29] P.Hohenberg, W.Kohn, Phys.Rev. **136B**, 864, (1964).

[30] N.D.Mermin, Phys.Rev. **137A** 1441 (1964).

[31] C. Ullrich, E.K.U. Gross, Aust. J. Phys., (1995), in press.

[32] A.J. Legget, Rev. Mod. Phys. **47**, 331, (1975).